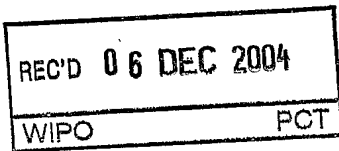




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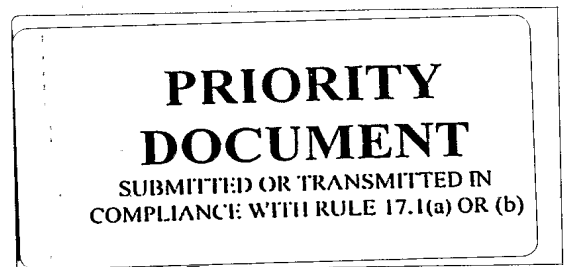
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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03078313.8



Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03078313.8
Demande no:

Anmeldetag:
Date of filing: 21.10.03
Date de dépôt:

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Composition for reducing NOx emissions

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C10G/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

ACH 3019 PDEP

COMPOSITION FOR REDUCING NO_x EMISSIONS

The present invention relates to a composition suitable for reducing NO_x emissions during catalyst regeneration in a fluid catalytic cracking (FCC) process, a process for preparing said composition, and its use.

In a fluid catalytic cracking process the catalyst particles circulate between a catalytic cracking zone and a regeneration zone. During regeneration, coke deposits formed on the catalyst during the cracking reaction are burnt away, resulting in environmentally undesired gases being emitted from the regeneration zone, e.g. SO_x, NO_x, and CO. Much effort is put on finding compositions which reduce said emissions. These compositions are added to the FCC unit either as an integral part of the FCC catalyst, or as separate particles. Mg-Al spinel containing compositions are frequently mentioned as suitable for SO_x and/or NO_x reduction.

WO 01/12570 discloses a composition comprising Mg-Al anionic clay and cerium. This composition is prepared by first mixing gibbsite and magnesium oxide in water to form an aqueous slurry, followed by adding cerium nitrate, and aging the resulting mixture, thereby forming some anionic clay. The product is subsequently spray-dried, calcined, and aged in order to obtain the desired composition.

This document further suggests that such compositions can be used as SO_x and/or NO_x-reducing additives in FCC.

25

The present invention provides a composition with improved NO_x-reducing capacity. The composition according to the invention comprises

- (a) a Mg and Al-containing component,
- (b) a rare earth metal oxide, and
- (c) an acidic oxide component.

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ACH 3019 PDEP

2

Preferably, the catalyst is in the form of fluidizable particles, i.e. particles having a particle size of about 20-200 microns.

5 Mg and Al-containing components include Mg and Al-containing anionic clays and heat-treated forms thereof, such as solid solutions and spinel. Mg and Al-containing anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of magnesium and aluminium hydroxides between which there are water molecules and anions. Suitable anions are NO_3^- , OH^- , Cl^- , Br^- , I^- , SO_4^{2-} , SiO_3^{2-} , CrO_4^{2-} , BO_3^{2-} , MnO_4^- , HGao_3^{2-} ,
10 HVO_4^{2-} , ClO_4^- , BO_3^{2-} , pillaring anions such as $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{Mo}_7\text{O}_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, and alkyl sulphonates such as laurylsulphonate.

Hydrotalcite is an example of a naturally occurring Mg and Al-containing anionic clay, in which carbonate is the predominant anion present. Meixnerite is a Mg
15 and Al-containing anionic clay wherein hydroxyl is the predominant anion present.

In the prior art, anionic clays are also referred to as hydrotalcite-like materials or layered double hydroxides. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double
20 hydroxide materials.

A characteristic of Mg-Al anionic clays is that mild calcination results in the formation of a disordered MgO-like product. Said disordered MgO-like product is distinguishable from spinel (which results upon severe calcination) and from
25 anionic clays. In this specification we refer to said disordered MgO-like materials as Mg-Al solid solutions. Furthermore, these Mg-Al solid solutions are characterised by a so-called memory effect whereby the exposure to water of such calcined materials results in the reformation of the anionic clay structure.

30 The Mg and Al-containing anionic clay does not necessarily consist of pure anionic clay. It may also be a component comprising the anionic clay and an aluminium or magnesium compound. This aluminium or magnesium compound

ACH 3019 PDEP

3

can be the starting material used for the anionic clay preparation, or reacted forms thereof, as long as they are not reacted to anionic clay. Hence, the compositions may contain some magnesium oxide, (pseudo)boehmite, brucite, aluminium trihydrate, or mixtures thereof.

5

Rare earth metal oxides which can suitably be used in the composition according to the invention are CeO_2 , and La_2O_3 .

10 The acidic oxide component is preferably selected from the group consisting of alumina, silica-alumina, Y-type aluminosilicate, and combinations thereof. It is even more preferred to use more than one acidic oxide, e.g. Y-type aluminosilicate and alumina, Y-type aluminosilicate and silica-alumina, or Y-type aluminosilicate and alumina and silica-alumina.

15 Examples of aluminas are boehmite, pseudoboehmite, gamma alumina, and heat-treated forms thereof.

A preferred Y-type aluminosilicate is zeolite Y with a Silica to Alumina Ratio (SAR) of less than 6, which preferably has been exchanged with rare earth (RE): REY zeolite.

- 20 Preferably, the composition according to the invention comprises
- (a) a Mg and Al-containing component in an amount of about 50-65 wt.%,
 - (b) CeO_2 in an amount of about 6-12 wt.%,
 - (c) alumina in an amount of about 25-35 wt.%,
 - (d) silica in an amount of 2-8 wt%, and
 - 25 (e) a REY zeolite in an amount of about 3-8 wt.%.

In a more preferred embodiment, the Mg and Al-containing component is a Mg-Al anionic clay.

- 30 The compositions according to the invention can be prepared by a process comprising the following steps:

ACH 3019 PDEP

4

- (1) combining an aluminium source with a magnesium source - at least one of them being water-insoluble - in water to form an aqueous slurry;
- (2) optionally milling the slurry,
- (3) aging the slurry,
- 5 (4) combining a precursor of the rare earth metal oxide with the product of step (3),
- (5) spray-drying the product of step (4),
- (6) calcining the spray-dried material,
- (7) optionally slurrying the product of step (6) in water and milling the
- 10 resulting slurry,
- (8) combining the product of step (6) or (7) with the acidic oxide component or a precursor thereof, and
- (9) shaping, preferably spray-drying the product of step (8).

- 15 Suitable aluminium sources include aluminium oxides and hydroxides such as transition alumina, aluminium trihydrate (gibbsite, bayerite) and its thermally treated forms (including flash calcined alumina), sols, amorphous alumina, (pseudo)boehmite, aluminium-containing clays such as kaolin, sepiolite, hydrotalcite, and bentonite, modified clays such as metakaolin, alumina salts
- 20 such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, sodium aluminate.

Aluminium trihydrate includes crystalline aluminium trihydrate (ATH), for example gibbsites provided by Reynolds Aluminium Company RH-20® or JM Huber Micral® grades. Also BOC (Bauxite Ore Concentrate), bayerite and

25 nordstrandite are suitable aluminium trihydrates. BOC is the cheapest alumina source. The aluminium trihydrate is preferred to have a particle size ranging from 1 to 150 µm, more preferably from 1 to 20 µm.

- Suitable magnesium sources include magnesium oxides or hydroxides such as
- 30 MgO, Mg(OH)₂, hydromagnesite, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy acetate, magnesium carbonate,

ACH 3019 PDEP

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magnesium hydroxy carbonate, magnesium bicarbonate, magnesium nitrate, magnesium chloride, magnesium-containing clays such as dolomite, saponite, and sepiolite, and mixtures of the above-mentioned magnesium sources.

- 5 The use of aluminium trihydrate as the aluminium source and magnesium oxide as the magnesium source is preferred.

The Mg/Al ratio may vary from 1 to 10, preferably from 1 to 6, most preferably from 2 to 4.

10

In this specification the term 'milling' is defined as any method that results in reduction of the particle size. Such a particle size reduction can at the same time result in the formation of reactive surfaces and/or heating of the particles. Instruments that can be used for milling include ball mills, high-shear mixers, colloid mixers, and electrical transducers that can introduce ultrasound waves into a slurry. Low-shear mixing, i.e. stirring that is performed essentially to keep the ingredients in suspension, is not regarded as 'milling'.

15

After the optional milling step (7), the particle size is preferably below 6 microns, more preferably below 3 microns.

20

During aging step (3), part of the aluminium and magnesium source may react to form an anionic clay. If the final composition is desired to contain anionic clay, the amount of anionic clay formed during step (3) is preferably between 5 and 75%, more preferably 5-25%, and most preferably 5 and 10 wt% of the final amount of anionic clay, because then shaped bodies with the highest physical strength are obtained.

25

The calcination step (6) is preferably performed at temperatures between 200° and 1000°C, more preferably between 300° and 800°C and most preferably between 400° and 600°C. Calcination is conducted for 15 minutes to 24 hours, preferably 1-12 hours and most preferred 2-6 hours. By this treatment a Mg and

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ACH 3019 PDEP

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Al-containing solid solution or a spinel is formed, depending on the exact calcination conditions.

The so-formed solid solution can be rehydrated to form an anionic clay again in step (7). This rehydration can be performed by contacting the solid solution with
5 water for 1-24 hours at thermal or hydrothermal conditions, preferably at temperatures ranging from 65°-85°C. Preferably, the slurry has a solids content ranging from about 10 to 50 wt%. Optionally, this rehydration can be performed in the presence of metal ions, e.g. Cu or Ba.

10 The compositions according to the invention exhibit good NO_x reducing properties in, e.g., FCC units. Therefore, the invention also relates to the use of the catalyst composition according to the invention for the reduction of NO_x emissions in FCC units.

The temperature in the catalytic cracking zone of the FCC unit is generally in
15 the range 375° to 650°C, more particularly 460° to 560°C. The pressure in this zone is generally between atmospheric pressure and a pressure of 7 atmospheres, more particularly between 1 and 3 atmospheres. In the regeneration zone, the catalyst is regenerated with an oxygen-containing gas at a temperature of about 540° to 825°C, more particularly 700° to 750°C and in
20 the pressure of steam.

The composition according to the invention is used in the FCC process in combination with a conventional FCC catalyst. The composition according to the invention and the FCC catalyst can be collectively incorporated into a matrix, thereby creating one type of catalyst particle. On the other hand, a
25 physical mixture of two types of particles can be used: particles comprising the composition according to the invention and FCC catalyst particles. This has the advantage that the amount of the composition according to the invention to be added to the FCC unit can be easily adapted to the specific conditions in the unit and the hydrocarbon feed to be processed.

ACH 3019 PDEP

7

CLAIMS

1. A composition comprising
 - a) a Mg and Al-containing component,
 - 5 b) a rare earth metal oxide, and
 - c) an acidic oxide component.
2. A composition according to claim 1, wherein the acidic oxide component is selected from the group consisting of Y-type aluminosilicate, alumina, silica-alumina, and combinations thereof.
10
3. A composition according to claim 2 comprising
 - a) a Mg and Al-containing component,
 - b) a rare earth metal oxide,
 - 15 c) alumina and/or silica-alumina, and
 - d) Y-type aluminosilicate.
4. A composition according to claim 3 comprising
 - a) a Mg and Al-containing component in an amount of about 50-65 wt.%,
20
 - b) CeO_2 in an amount of about 8-12 wt.%,
 - c) alumina in an amount of about 25-35 wt.%,
 - d) silica in an amount of 2-8 wt%, and
 - e) a REY zeolite in an amount of about 2-10 wt.%.
25
5. A composition according to any one of the preceding claims wherein the Mg and Al-containing component is a Mg-Al anionic clay.
6. A composition according to any one of the preceding claims which
30 additionally comprises Cu.

ACH 3019 PDEP

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7. A process for preparing a composition according to any one of the preceding claims, comprising
- (1) combining an aluminium source and a magnesium source in water to form an aqueous slurry;
 - 5 (2) optionally milling the slurry,
 - (3) aging the slurry,
 - (4) combining a precursor of the rare earth metal oxide with the product of step (3),
 - (5) spray-drying the product of step (4),
 - 10 (6) calcining the spray-dried material,
 - (7) optionally slurrying the product of step (6) in water and milling the resulting slurry,
 - (8) combining the product of step (6) or (7) with the acidic oxide component, and
 - 15 (9) shaping the product of step (8).
8. Process according to claim 7 wherein the aluminium source is aluminium trihydrate and the magnesium source is magnesium oxide.
- 20 9. Use of the composition according to any one of claims 1-6 for reducing NO_x emissions in an FCC unit.

ACH 3019 PDEP

9

ABSTRACT

The invention relates to a composition suitable for reducing NO_x emissions during, e.g., catalyst regeneration in a fluid cracking cracking process, said
5 composition comprising a Mg and Al-containing component, a rare earth metal oxide, and an acidic oxide component. The invention further relates to a process for preparing such a composition and its use for reducing NO_x emissions.

PCT/EP2004/011457

